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(54) THIN FILM AND ANTIREFLECTION FILM USING THE SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To prepare a thin film having micro voids and an excellent antireflection property by preparing a film comprising a binder resin which contains a fluorine compound and an organic silicon compound as main components and a small particle.

SOLUTION: As a fluorine compound, one having at least two polymerizing functional groups is preferable. An organic silicon compound, $Si(R1)i(r2)j(r3)k(OR4)4-(i+j+k)$ (wherein R1, R2 and R3 are each an organic group having at least one of H, O and F; R4 is an aliphatic, an alicyclic or an aromatic residue; (i), (j), (k) are each 0 or 1) is preferable. As a small particle, an inorganic oxide containing an element selected from Si, Al, Sn, Sb, Zn and Ti and an emulsion particle of magnesium fluoride, calcium fluoride or an organic compound can be used, but inorganic small particles are preferable. Usually 5-200 pts.wt. of a small particle is used against 100 pts.wt. of a binder resin. A thin film is obtained by dispersing or dissolving small particle and a binder and carrying out coating.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]**[0001]**

[Field of the Invention] This invention The cathode-ray tube of television, the antireflection film for liquid crystal displays, the antireflection film of various displays, such as an acid-resisting filter for CRT monitors, It is related with the thin film used suitably for antireflection films, such as a case for exhibition, a show window and the frame of pictures, a windowpane, an optical lens, and a glass lens, etc., and the antireflection film using it. It can also use as a semiconductor-related low dielectric.

[0002]

[Description of the Prior Art] Acid resistibility articles, such as a filter for acid resisting used for a display etc., provide the optical thin film of a low refractive index in a substrate by a monolayer, or provide the optical thin film of a high refractive index and a low refractive index in a multilayer by turns, and make it the antireflection layer in many cases.

[0003] As a method of obtaining such an optical thin film, it is common to laminate an inorganic substance to a substrate by vacuum evaporation, weld slag, etc., and the antireflection film produced by doing in this way is excellent in low reflection at abrasion-proof nature. However, although the antireflection layer with highly efficient vacuum evaporation and method of carrying out weld slag and carrying out acid-resisting processing was obtained in the inorganic substance, since the large-scale device which needs a vacuum was used, productivity was bad and the manufacturing cost's was expensive. The substrate which can use these methods from a heat-resistant point etc. since a substrate is heated by not less than 80 ** at the time of vacuum evaporation or weld slag was limited.

[0004] After dissolving the organic substance of a low refractive index in a solvent, the method of coating a substrate with the organic substance of a low refractive index, forming a low-refractive-index organic thin film, and using as an antireflection film came to be learned in

recent years. Such a solution coating method is indicated by JP,4-355401,A, JP,6-18705,A, etc., for example. The low-refractive-index substance used with these solution coating method is resin with high fluoride content.

The outstanding acid-resisting characteristic is shown.

Since these form a thin film by solution coating, unlike vacuum evaporation or the method of carrying out weld slag and carrying out acid-resisting processing, they can form an antireflection film with sufficient productivity for an inorganic oxide.

[0005]However, although the acid-resisting characteristic which was excellent since solution coating was possible for the organic thin film which becomes JP,4-355401,A or JP,6-18705,A from fluorine-containing resin of a statement, and productivity was good and a low refractive index is shown, There was a problem that these fluorine-containing resin curing things have low surface hardness since crosslinking density is low, and it was inferior to abrasion-proof nature.

[0006]It is insoluble to a solvent, and although the hardened material of the perfluoro divinyl ether in which surface hardness is indicated by USP,3,310,606 as high, high fluorine-containing resin of crosslinking density is mentioned, since it is necessary to mold this hardened material under an elevated temperature and high voltage, it cannot obtain an optical thin film.

[0007]On the other hand, although the air bubbles below wavelength are formed in the inside of polymer given in JP,4-121701,A and the antireflection film in which the refractive index used the principle of the heterogeneous film which changes to a thickness direction continuously is indicated, Since the inquiry process of the solvent soluble component by solvent cleaning was included in formation of a micro opening, there was a problem that it was difficult for a refractive index to obtain the film which changed continuously.

[0008]Although the antireflection film which forms a low refractive index layer including a micro opening with an opposite phase emulsification method into the thin film which consists of resin is indicated to JP,9-227713,A, It was not necessarily in process an easy method because of the dispersing process which forms the emulsion which made the particle diameter below the wavelength of visible light distribute water with a dispersion machine being required, and there being etc.

[0009]

[Problem(s) to be Solved by the Invention]This invention tends to cancel the fault of the above-mentioned conventional technology.

The purpose is to provide the antireflection film using the thin film and this which could form with the simple technique and were excellent also in surface hardness.

[0010]

[Means for Solving the Problem]To achieve the above objects, this invention has the following

composition.

[0011]1. Thin film which is thin film which has binder resin which uses fluorine compound and organosilicon compound as the main ingredients, and particles, and is characterized by having micro opening.

[0012]2. Antireflection film characterized by coming to form the thin film concerned on film whose refractive index is higher than the thin film concerned.

[0013]

[Embodiment of the Invention]In the thin film of this invention, having a micro opening has the feature. It is suitably used in many cases by being provided in the outermost surface of the transparent base material which should give acid resistibility, using this thin film as a low refractive index film. Here, a micro opening means all of the air layer formed by the microvoid in a film, or unevenness of a membrane surface. By this, if micro, it is a composite construction of a resin layer and an opening, but if macroscopic, it can be regarded as one layer, and the film of a low refractive index can be formed rather than usually expected.

[0014]Since the film which consists of particles and resin becomes a weighted average efficiency of those refractive indicees in the usual case, it is difficult to have sufficient low-refractive-index nature as it is.

[0015]However, since the refractive index of air is 1, in the thin film which has a micro opening of this invention, it can produce decline in refractive index much more than the film which only consists of particles and resin. That is, the low refractive index film which has a micro opening comes between the refractive indicees of the film which consists of the refractive index, resin, and the particles of an air layer. Therefore, the refractive index of the thin film of this invention can make only the part of the volume fraction of a micro opening lower than the refractive index presumed from each raw material.

[0016]The layer which has such a low refractive index can also be further used as the top layer of a multilayer film not only as monolayer. By multilayering, obtaining an effective antireflection film in a larger wavelength area is based on the same publicly known principle as a Prior art.

[0017]As for the content of a micro opening, when the ratio of the micro opening in a film is too high, there is a tendency which spoils membranous physical intensity and it is preferred to consider it as 50% or less with a volume fraction. Although the size of a micro opening does not have limitation in particular, when you need membranous physical intensity, it is preferred that it is 2/3 or less to thickness.

[0018]Even if the fluorine compound used as binder resin of the thin film of this invention is easy for the dispersibility of particles mentioned later and is not usually constructing a bridge from a point of film strength at the time of coating, it can use conveniently what changes into the state where the bridge was constructed after coating. Usually, as a typical fluorine-containing compound used for such a purpose, it is preferred to have a polymerization nature

functional group in a molecule, and it is having two or more functional groups more preferably. It is still more preferred that this fluorine compound has at least one sort chosen from a (meth) acryloyloxy group, a vinyl group, an epoxy group, and a vinyl ether group as a polymerization nature functional group from the point that composition is still easier. It is because these functional groups can form the structure of cross linkage easily by heat or light. The example is given to below.

[0019] As a fluoride content (meta) acrylate compound, Aliphatic series, alicycle fellows, and aromatic system fluoride content mono- (meta) acrylate. For example, 2,2,2-trifluoroethyl (meta) acrylate, 2,2,3,3,3-pentafluoro propyl (meta) acrylate, 2-(perfluoro butyl) ethyl (meta) acrylate, 3-perfluoro butyl-2-hydroxypropyl (meta) acrylate, 2-(perfluoro hexyl) ethyl (meta) acrylate, 3-perfluoro hexyl-2-hydroxypropyl (meta) acrylate, 2-(perfluoro octyl) ethyl (meta) acrylate, 3-perfluoro octyl-2-hydroxypropyl (meta) acrylate, 2-(perfluoro decyl) ethyl (meta) acrylate, 2-(perfluoro 3-methylbutyl) ethyl (meta) acrylate, 3-(perfluoro 3-methylbutyl)-2-hydroxypropyl (meta) acrylate, 2-(perfluoro 5-methylhexyl) ethyl (meta) acrylate, 2-(perfluoro 9-methyloctyl) ethyl (meta) acrylate, 2-(perfluoro 9-methyldecyl) ethyl (meta) acrylate, 2,2,3,3-tetrafluoro propyl (meta) acrylate, 1H and 1H, 5H-octafluoropentyl (meta) acrylate, 1H,1H,7H-dodecafluoropentyl (meta) acrylate, 1H,1H,9H-hexadecafluorononyl (meta) acrylate, 1H,1H,11H-AIKOSA fluoroundecyl (meta) acrylate, 2,2,2-trifluoro-1-trifluoro methylethyl (meta) acrylate, 2,2,3,4,4,4-hexafluoro butyl (meta) acrylate, etc. are mentioned.

[0020] Polyfunctional fluoride content (meta) acrylate is especially used preferably by this invention, and the di(meth)acrylate which are shown with the following structural formula is mentioned as the example.

[0021]

$\text{CH}_2=\text{CRCOO. (CH}_2\text{) f. (CF}_2\text{) g. (CH}_2\text{) hOCOCR=CH}_2\text{CH}_2=\text{CRCOOCH}_2\text{CH(OH) (CH}_2\text{) f(CF}_2\text{)}$
 $\text{g(CH}_2\text{) hCH(OH) CH}_2\text{OCOCR=CH}_2\text{CH}_2=\text{CRCOOCH}_2\text{CH}_2\text{OCO. (CF}_2\text{)}$
 $\text{gCOOCH}_2\text{CH}_2\text{OCOCR=CH}_2\text{CH}_2=\text{CRCOOCH}_2\text{CH(OH) CH}_2\text{OCO(CF}_2\text{) gCOOCH}_2\text{CH(OH)}$
 $\text{CH}_2\text{OCOCR=CH}_2\text{CH}_2=\text{CRCOOHCOO. (CH}_2\text{) f. (CF}_2\text{) g. (CH}_2\text{) it is}$
 $\text{hOCOHCOCR=CH}_2\text{CH}_2=\text{CRCOOCH}_2\text{CH}_2\text{NHCOO(CH}_2\text{) f(CF}_2\text{) g(CH}_2\text{)}$
 $\text{hOCOHCOCR=CH}_2\text{CH}_2=\text{CRCOOCH}_2\text{CH}_2$. In the above-mentioned formula, R expresses H or CH_3 and, as for 0-2g, in f, 0-12h express the integer of 0-2. As for g, in order to reduce a refractive index and to hold a certain amount of hardness, being referred to as 4-10 is preferred. $\text{CH}_2=\text{CRCOO}$
 $(\text{CH}_2\text{) f(CF}_2\text{) g(CH}_2\text{) hOCOCR=CH}_2$ is more preferably used from a composite ease and a viewpoint of low-refractive-index nature.

[0022] In order to raise crosslinking density, in addition, ethyl (meta) acrylate, 2-hydroxy-3-phenoxypropylacrylate, Ethylhexyl (meta) acrylate, styrene, methylstyrene, Monofunctional

monomers, such as N-vinyl pyrrolidone, and polyfunctional monomer, For example, triethylene glycol di(metha)acrylate, poly ethylene glycol di(metha)acrylate, 1,6-nonanediol diacrylate, dimethylol tricyclodecane diacrylate, 2-methacryloiloxy-ethyl acid phosphate, TORIMECHI roll pro pantry (meta) acrylate, Hexandiol (meta) acrylate, Tori propyleneglycol di(meth) acrylate, Diethylene GURIKORUJI (meta) acrylate, penta ERIIS RITORUTORI (meta) acrylate, Pentaerythritol tetra (meta) acrylate, dipentaerythritol hexa (meta) acrylate, 1,6-hexanediol di (metha)acrylate, neopentyl glycol di(metha)acrylate, trimethylolpropan(meta) acrylic acid benzoic ester, 2-hydroxy-3-acryloyloxypropyl (meta) acrylate, Hydroxy pivalate neopentyl glycol di(metha)acrylate, Polytetramethylene GURIKORUJI (meta) acrylate and the compound which does not contain fluoride, such as trimethylolpropanetetra (meta) acrylate, 1,3-butanediol di(metha)acrylate, and 1,10-decane JIORUJI (meta) acrylate, at the time are also mixable.

[0023]Independent, it is mixed and these compounds are used.

[0024]Radical polymerization initiators, such as azo and a peroxide system, are used for these (meta) acrylate compounds, Preferably whether thermal polymerization is carried out on condition of under hypoxia concentration Acetophenones. As benzophenones, MIHIRA benzoyl benzoate, alpha-amylomaize Qeshm ester, tetramethylthiuram monosulfide, thioxants, and a photosensitizer, Optical radical polymerization initiators, such as n-butylamine, triethylamine, tri-n-butyl phosphines, ketals, and anthraquinone, are used.

[0025]In heat treatment, it must carry out below with the deformation temperature of this substrate. When performing live-wire energy ray processing, an electron beam or ultraviolet rays are usually used. Especially in the case of ultraviolet curing, the device which uses an ultrahigh pressure mercury lamp, a high-pressure mercury-vapor lamp, a low pressure mercury lamp, a xenon arc, a carbon arc, a metal halide lamp, etc. as a light source is used. It carries out by replacing oxygen in a system by inactive gas, such as nitrogen, depending on the case.

[0026]As a fluoride content epoxy compound, aliphatic series, alicyclic, an aromatic system fluoride content monofunctional epoxy compound, For example, hexafluoro epoxy propane, 3-perfluoro butyl-1,2-epoxypropane, 3-perfluoro hexyl-1,2-epoxypropane, 3-perfluoro octyl-1,2-epoxypropane, 3-perfluoro decyl-1,2-epoxypropane, 3-(perfluoro 3-methylbutyl)-1,2-epoxy propane, 3-(perfluoro 5-methylhexyl)-1,2-epoxy propane, 3-(perfluoro 7-methyloctyl)-1,2-epoxy propane, 3-(perfluoro 9-methyldecyl)-1,2-epoxy propane, 3-(2,2,3,3-tetrafluoro propoxy)-1,2-epoxy propane, 3-(1 H,1 H,5H-octafluoro pentyloxy)-1,2-epoxy propane, 3-(1 H,1 H,7H-dodecafluoro heptyloxy)-1,2-epoxy propane, 3-(1 H,1 H,9H-hexadecafluoro nonyloxy)-1,2-epoxy propane, etc. are mentioned.

[0027]Polyfunctional fluoride content epoxy compounds are especially used preferably by this invention, and the epoxy compounds shown with the following structural formula are mentioned as the example.

[0028]

Ep-CH -- $\text{O}_a(\text{CH}_2)_b(\text{CF}_2)_c(\text{CH}_2)_d(\text{O})_e\text{CH}_2$ -Ep -- however, Ep expresses the integer of an epoxy group, $a = 0\text{-}1$, $b = 0\text{-}2$, $c = 2\text{-}12$, $d = 0\text{-}2$, and $e = 0\text{-}1$.

[0029] in an upper type, c is or more 2 12 or less integer preferably, and as for c, in order to reduce a refractive index and to hold hardness and low-refractive-index nature, it is preferred to or more 4 use ten or less.

[0030]In order to raise crosslinking density, in addition, aliphatic series, alicyclic, an aromatic system monofunctional epoxy compound, Ethylene glycol diglycidyl ether, polyethylene glycol diglycidyl ether, Propylene glycol diglycidyl ether, polypropylene glycol diglycidyl ether, Hexahydro bisphenol A type diglycidyl ether, bisphenol A type (hydrogenation) diglycidyl ether, 2 and 2-dibromoneopentylglycol diglycidyl ether, Glycerin diglycidyl ether, trimethylolpropane triglycidyl ether, Phthalic acid diglycidyl ester, dimer acid diglycidyl ester, Polyfunctional epoxy compounds, such as triglycidyl isocyanurate, tetraglycidyl ether aminodiphenylmethane, and cresolnovolak poly glycidyl ether, an epoxy group content Silang system compound, etc. can also be added.

[0031]In the case of an epoxy compound, as a polymerization initiator, acid anhydrides, amines, amide, phenols, a mercapto compound (poly), imidazole derivatives, aromatic diazonium salt, a cation grant system, etc. are raised. As a photolysis cation grant system, proton acid, acid halogenation metal, an organic metallic compound, a stable carbonium ion salt, etc. are mentioned. The compound of a photolysis cation grant system fits hardening from the length of pot life, and the speed of the cure rate especially, Diaryliodonium salt, triaryl sulfonium salt, a triaryl seleno NIUMU salt, It is a simple substance, or triaryl pyrylium salt, benzylpyridiniumthiocyanate, dialkyl phenacyl sulfonium salt, dialkyl hydroxyphenyl sulfonium salt, dialkyl hydroxyphenyl phosphonium salt, an iron allene complex, etc. are mixed, and are used.

[0032]As a fluorine-containing vinyl ether compound, a multifunctional compound with the following structures besides monofunctional can be mentioned.

[0033]

$\text{CH}_2=\text{CH-O-CH}_2-\text{O-CH}=\text{CH}_2 \text{CH}_2=\text{CH-O-CH}_2-\text{O-CH}_2-(\text{CF}_2) \text{ k-CH}_2-\text{O-CH}_2-$
 $\text{O-CH=CH}_2 \text{CH}_2=\text{CH-O-CH}_2-\text{O-} (\text{CH}_2)_2-(\text{CF}_2) \text{ k-} (\text{CH}_2)_2-\text{O-CH}_2-\text{O-CH=CH}_2 \text{CH}_2=\text{CH-O-}$
 $\text{CH}_2-\text{O-(CH}_2)_3-(\text{CF}_2) \text{ k-(CH}_2)_3-\text{O-CH}_2-\text{O-CH=CH}_2 \text{CH}_2=\text{CH-O-} (\text{CH}_2)_2-\text{O-} (\text{CF}_2)_k-\text{O-}$
 $(\text{CH}_2)_2-\text{O-CH=CH}_2 \text{CH}_2=\text{CH-O-(CH}_2)_2-\text{O-CH}_2-(\text{CF}_2) \text{ k-CH}_2-\text{O-(CH}_2)_2-\text{O-CH=CH}_2 \text{CH}_2=\text{CH-O-}$
 $(\text{CH}_2)_2-\text{O-(CH}_2)_2-(\text{CF}_2) \text{ k-} (\text{CH}_2)_2-\text{O-} (\text{CH}_2)_2-\text{O-CH=CH}_2 \text{CH}_2=\text{CH-O-(CH}_2)_2-\text{O-(CH}_2)_3-$
 $(\text{CF}_2) \text{ k-(CH}_2)_3-\text{O-(CH}_2)_2-\text{O-CH=CH}_2$ In addition, in the above-mentioned formula, k is or more
 $2-12$ or less integer preferably, and in order to reduce a refractive index and to hold a certain

amount of hardness, it is preferred [k] to or more 4 use ten or less.

[0034]The vinyl ether compound which does not contain fluoride in order to raise crosslinking density, For example, aliphatic series, alicycle fellows, an aromatic system monofunctional vinyl ether compound, 1,3-pro pansy ORUJI vinyl ether, 2-methyl-1,3-pro pansy ORUJI vinyl ether, diethylene-glycol divinyl ether, Two organic functions, such as butanediol divinyl ether and hexandiol divinyl ether, or the vinyl ether compound beyond it, a vinyl ether group content Silang system compound, the vinyl ether compound containing fluoride, etc. can also be added.

[0035]As a hardening agent of a vinyl ether group, the compound of a cation grant system is used preferably. As a compound of a cation grant system, proton acid, acid halogenation metal, an organic metallic compound, a stable carbonium ion salt, etc. are mentioned. The compound of a photolysis cation grant system fits hardening from the length of pot life, and the speed of the cure rate especially, Aromatic diazonium salt, diaryliodonium salt, triaryl sulfonium salt, A triaryl seleno NIUMU salt, triaryl pyridinium salt, a benzylpyridinium thioisocyanate, Dialkyl phenacyl sulfonium salt, dialkyl hydroxyphenyl sulfonium salt, dialkyl hydroxyphenyl phosphonium salt, a metallocene compound, etc. are mentioned.

[0036]It is desirable at the point that what is generally shown with the following structure can form the structure of cross linkage as an example of the organosilicon compound used as binder resin of the low refractive index film of this invention.

[0037] $\text{Si}(\text{R1})_i(\text{R2})_j(\text{R3})_k(\text{OR4})_{4-(i+j+k)}$ -- here, R1, R2, and R3 express the organic group containing at least one chosen from hydrogen, oxygen, and a fluorine atom. R4 expresses at least one chosen from aliphatic series, alicycle fellows, and aromatic residue. As for i= 0 or 1, and j, 0 or 1k expresses the integer of 0 or 1, respectively. As an example, methylsilicate, ethyl silicate, n-propylsilicate, Tetra alkoxy silane and hydrolyzates of those, such as i-propylsilicate, n-butylsilicate, sec-butylsilicate, and t-butylsilicate, Furthermore, methyl trimetoxysilane, methyl triethoxysilane, methyltriacetoxysilane, MECHIRUTORI butoxysilane, ethyltrimethoxysilane, ethyltriethoxysilane, Vinyltrimetoxysilane, vinyltriethoxysilane, vinyltriacetoxysilane, A vinyl trimethoxy ethoxysilane, a vinyl dimethylethoxy silane, Vinylmethyl diethoxysilane, phenyltrimethoxysilane, phenyltriethoxysilane, Phenyl triacetoxysilane, gamma-chloropropyltrimetoxysilane, gamma **KURORO propyl triethoxysilane, gamma **KURORO propyl triacetoxysilane, 3,3,3-trifluoro propyltrimetoxysilane, gamma-methacryloxypropyltrimetoxysilane, gamma **AMINO propyltrimetoxysilane, gamma **AMINO propyl triethoxysilane, gamma **MERUKAPUTO propyltrimetoxysilane, gamma **MERUKAPUTO propyl triethoxysilane, N-beta-(aminoethyl)-gamma **AMINO propyltrimetoxysilane, beta **SHIANO ethyltriethoxysilane, methyl triphenoxy silane, Chloromethyl trimethoxysilane, chloromethyl triethoxysilane, Glycidoxymethyltrimetoxysilane, glycidoxymethyl triethoxysilane, alpha **GURISHIDOKISHI ethyltrimetoxysilane, alpha

**GURISHIDOKISHI ethyltriethoxysilane, beta **GURISHIDOKISHI ethyltrimethoxysilane, beta
**GURISHIDOKISHI ethyltriethoxysilane, alpha **GURISHIDOKI Cipro pill trimethoxysilane,
alpha **GURISHIDOKI Cipro pill triethoxysilane, beta **GURISHIDOKI Cipro pill
trimethoxysilane, beta **GURISHIDOKI Cipro pill triethoxysilane, Gamma-
glycidoxypyropyltrimetoxysilane, gamma **GURISHIDOKI Cipro pill triethoxysilane, Diethoxy-3-
glycidoxypyropylmethylsilane, dimethoxy- 3-glycidoxypyropylmethylsilane, 3-glycidoxypyropyl
dimethoxysilane, gamma-(meta) acryloyloxypropyl dimethylethoxy silane, gamma-(meta)
acryloyloxypropyl methyldiethoxysilane, gamma **GURISHIDOKISHI propyl tripropoxy silane,
gamma **GURISHIDOKISHI PUROPIRUTORI butoxysilane, gamma
**GURISHIDOKISHI PUROPIRUTO trimethoxy ethoxysilane, gamma **GURISHIDOKI Cipro pill
triphenoxysilane, alpha **GURISHIDOKISHI butyltrimethoxysilane, alpha **GURISHIDOKISHI
epoxybutyltriethoxysilane, beta **GURISHIDOKISHI butyltrimethoxysilane, beta
**GURISHIDOKISHI epoxybutyltriethoxysilane, gamma **GURISHIDOKISHI
butyltrimethoxysilane, gamma **GURISHIDOKISHI epoxybutyltriethoxysilane, delta
**GURISHIDOKISHI butyltrimethoxysilane, delta **GURISHIDOKISHI
epoxybutyltriethoxysilane, (3,4-epoxycyclohexyl) Methyl trimetoxysilane, methyl (3,4-
epoxycyclohexyl) triethoxysilane, beta-(3, 4-epoxycyclohexyl) ethyltrimethoxysilane, beta-(3,4-
epoxycyclohexyl) ethyltriethoxysilane, beta-(3,4-epoxycyclohexyl) ethyl tripropoxy silane, beta-
(3, 4-epoxycyclohexyl) ECHIRUTORI butoxysilane, beta-(3,4-epoxycyclohexyl) ethyl
trimethoxy ethoxysilane, beta-(3,4-epoxycyclohexyl) ethyl triphenoxysilane, gamma-(3, 4-
epoxycyclohexyl) propyltrimethoxysilane, gamma-(3,4-epoxycyclohexyl) propyl triethoxysilane,
delta-(3, 4-epoxycyclohexyl) butyltrimethoxysilane, Trialkoxysilane, such as delta-(3, 4-
epoxycyclohexyl) epoxybutyltriethoxysilane, doria -- a sill oxysilane, triphenoxysilane or the
hydrolyzate of those, and dimethyldimethoxysilane. Phenylmethyldimethoxysilane, dimethyl
diethoxysilane, phenylmethyldiethoxysilane, gamma **KURORO propylmethyl
dimethoxysilane, gamma-chloropropyl methyldiethoxysilane, Dimethyldi acetoxysilane,
gamma-methacryloxypropylmethyldimethoxysilane, Gamma-
methacryloxypropylmethyldiethoxysilane, gamma-mercaptopropylmethyl dimethoxysilane,
gamma **MERUKAPUTO propylmethyl diethoxysilane, gamma **AMINO propylmethyl
dimethoxysilane, gamma **AMINO propylmethyl diethoxysilane, methylvinyl dimethoxysilane,
Methylvinyl diethoxysilane, glycidoxypyropylmethyldimethoxysilane, Glycidoxypyropyl
methyldiethoxysilane, alpha **GURISHIDOKISHI ethyl methyl dimethoxysilane, alpha
**GURISHIDOKISHI ethyl methyldiethoxysilane, beta **GURISHIDOKISHI ethyl methyl
dimethoxysilane, beta **GURISHIDOKISHI ethyl methyldiethoxysilane, alpha **GURISHIDOKI
Cipro pill methyl dimethoxysilane, alpha **GURISHIDOKI Cipro pill methyldiethoxysilane, beta
**GURISHIDOKI Cipro pill methyl dimethoxysilane, beta **GURISHIDOKI Cipro pill
methyldiethoxysilane, gamma **GURISHIDOKI Cipro pill methyl dimethoxysilane, Gamma-

glycidoxypyropylmethyldietoxysilane, gamma **GURISHIDOKISHI propyl methyldi propoxysilane, gamma **GURISHIDOKISHI propylmethyl dibutoxysilane, gamma **GURISHIDOKISHI PUROPIRU methyldi methoxyethoxy silane, gamma **GURISHIDOKISHI propylmethyl diphenoxysilane, gamma **GURISHIDOKISHI propylethyl dimethoxysilane, gamma **GURISHIDOKI Cipro pill ethyldiethoxysilane, gamma **GURISHIDOKISHI propylethyl dipropoxysilane, gamma **GURISHIDOKI Cipro pill vinyldimetoxysilane, gamma **GURISHIDOKISHI propylvinyl diethoxysilane, gamma **GURISHIDOKISHI propylphenyl dimethoxysilane, Dialkoxy silanes, such as gamma **GURISHIDOKISHI propylphenyl diethoxysilane, or diacyloxysilanes. A tetramethoxy silane, a tetraethoxysilane, tetra-iso-propoxysilane, Tetra-n-propoxysilane, tetra-n-butoxysilane, tetra-sec-butoxysilane, Tetra-tert-butoxysilane, a tetra pentaethoxy silane, Tetrapenta- iso-propoxysilane, tetrapenta- n-propoxysilane, Tetrapenta- n-butoxysilane, tetrapenta- sec-butoxysilane, Tetrapenta- tert-butoxysilane, a methyl tripropoxy silane, A dimethylethoxy silane, dimethyl methoxysilane, dimethyl propoxysilane, Silane compounds, such as dimethyl butoxysilane, methyl dimethoxysilane, hexyl trimethoxysilane, and gamma-(meta) acryloyloxypropyl trimethoxysilane, or the hydrolyzate of those is the example.

[0038]Hydrolysis is attained by adding and agitating aqueous acids, such as pure water or chloride, acetic acid, or sulfuric acid. It is also easily possible by furthermore adjusting the addition of pure water or aqueous acids to control the degree of hydrolysis. Especially when hydrolyzing, it is [a hydrolytic basis and more than equimolar] desirable in respect of the promotion of hardening of the pure water below a 3 time mol or addition of aqueous acids.

[0039]In addition, it may be an organosilicon compound which contains polymerization nature functional groups, such as an epoxy group, in the middle of a chain.

[0040]These compounds can also be added [one sort or] by two or more sorts. In particular, in the structure of the above-mentioned organosilicon compound, it is more preferably used from the field of membranous intensity that any one or more of R1, R2, or the R3 have a polymerization nature functional group.

[0041]It is more preferably used in that it has high reactivity that any one or more of R1, R2, or the R3 are a (meth)acryloyloxy group, a vinyl group, an epoxy group, or a vinyl ether group.

[0042]Especially the organosilicon compound that has the epoxy group or (meth)acryloyloxy group which may polymerize easily with heat or an electron beam in a molecule before long is preferred.

[0043]As what can form a polymerization nature functional group and chemical bonds, such as an acrylate compound (meta), an epoxy compound, and a vinyl ether compound, as an example, and an example, Vinyltriethoxysilane, gamma-(meta) acryloyloxypropyl trimethoxysilane, gamma-aminopropyl trimethoxysilane, gamma-mercapto propyltrimethoxysilane, Gamma-glycidoxypyropyltrimetoxysilane, gamma-glycidox

propyltriethoxsilane, gamma-glycidoxy ethyl trimethoxy silane, gamma-glycidoxy propyl methyldimethoxsilane, etc. are more preferred.

[0044]As an example of the organosilicon compound which has an epoxy group, the following are used preferably.

[0045]

$(Ep-CH_2O(CH_2)_l)_mSi(R5)_n(R6)_p(OR7)_{4-(m+n+p)}$ however R5, and R6 express the organic group containing at least one chosen from hydrogen, oxygen, and a fluorine atom. R7 expresses at least one chosen from aliphatic series, alicycle fellows, and aromatic residue. As for 0-4m, in l, 0-3p express the integer of 0-3, respectively, as for 0-3n.

[0046]As an example of the organosilicon compound which has a (meth)acryloyloxy group, the following are used preferably.

[0047]

$(CH_2=CRCOO(CH_2)_q)_rSi(R8)_s(R9)_t(OR10)_{4-(r+s+t)}$ however R8, and R9 express the organic group containing at least one chosen from hydrogen, oxygen, and a fluorine atom. R10 expresses one chosen from aliphatic series, alicycle fellows, and aromatic residue. As for 0-4r, in q, 0-3t express the integer of 0-3, respectively, as for 0-3s.

[0048]In addition, an one end vinyl functionality polysilane compound with a polymerization sexual response group, Both-ends vinyl functionality polysilane, an one end vinyl functional polysiloxane, a both-ends vinyl functional polysiloxane, the vinyl functionality polysilane to which these compounds were made to react, or a vinyl functional polysiloxane is raised.

[0049]The hardening method usually according [these] to heat is used. Use of various metal alkoxides, such as alkali metal salt of carboxylic acid, aluminum, titanium, and a zirconium, or chelate compound is raised in order to bring a cure rate forward.

[0050]When the Silang system compound and an epoxy compound are used together, if various metal chelate compound, such as aluminum, titanium, a zirconium, iron, and copper, is used as a hardening agent, since both can be hardened simultaneously, it is desirable.

[0051]The aluminum chelate compound which metal chelate compound can use for the purpose of the invention in this application conveniently also in these hardening agents, and is especially shown in the following from points, such as the stability of a paint, is useful.

[0052]An aluminum chelate compound here is an aluminum chelate compound shown, for example by general formula $AlX_{V}Y_{3-V}$.

[0053]However, as for the inside of a formula, and X, OL (L is a low-grade alkyl group) and Y are general formula $M^1COCH_2COM^2$ (M^1). ligand [originating in the compound shown by M^2 (each -- a low-grade alkyl group)], and general formula $M^3COCH_2COOM^4$ (M^3 --) [3 and]

Each M^4 is at least one chosen from the ligand originating in the compound shown by a low-

grade alkyl group, and V is 0, 1, or 2.

[0054]As an aluminum chelate compound shown by general formula AlX_VY_{3-V} , although various compounds can be mentioned, Especially a desirable thing from viewpoints of the solubility to a constituent, stability, etc., They are aluminum acetylacetone, aluminum bis-ethylacetacetate monoacetyl acetone, aluminum di-n-butoxide mono ethyl acetoacetate, aluminum di-iso-propoxide monoethyl acetoacetate, etc. These can also mix and use two or more sorts. In that case, an acetylacetone can also be added into a paint solvent from a point of the storage stability of a paint. In addition, although various epoxy resin hardeners or various organic silicone hardening agents are used, as for these compounds, about 0.1-20 weight is used to a total of 100 weight sections of an epoxy compound and the Silang system compound.

[0055]Here, composition ratio with each preferred binder component in this invention at the time of making these whole binder component into 100 weight sections is described.

[0056]One to fluorine compound 99 weight section and 99 to organosilicon compound 1 weight section are preferred as a binder component. They are ten to fluorine compound 90 weight section, and 90 to organosilicon compound 10 weight section more preferably. They are the fluorine compound 20 - the amount part of 80, and 80 to organosilicon compound 20 weight section still more preferably. A fluorine compound is because there is a tendency for membranous intensity to run short, in less than ten weight sections when the tendency hardly seen has decline in a refractive index and it exceeds 90 weight sections.

[0057]As particles used for the thin film of this invention, that whose itself is a low refractive index comparatively is preferred, The emulsion particle of the inorganic oxide containing one or more sorts of elements of an inorganic system chosen from Si, aluminum, Sn, Sb, Zn, and Ti at least, magnesium fluoride, calcium fluoride, and an organic system is mentioned. The particles of an inorganic system are preferred. Hayes of the film formed when it exceeded 1 nm or more of mean particle diameter [100 nm or less of] of 100 nm, although the mean particle diameter measured with the BET adsorption method of these particles was 5-40 nm preferably becomes large, and there is a tendency which is inferior in transparency. Although it usually uses with the gestalt of sol when using these particles, in order to obtain sol with higher dispersibility, the thing which carrier fluid, such as water, alcohol, ester, and hydrocarbon, was made to distribute is usually used. these particles receive binder resin 100 weight section in a low refractive index film -- five weight sections - 200 weight sections -- desirable -- 15 weight sections - 150 weight-section *****. To binder resin 100 weight section, when more than less than five weight sections or 150 weight sections, a void cannot do quantity of particles easily, and there is a tendency for decline in a refractive index to no longer be seen.

[0058]The particles of this invention, a binder, and the hardening agent and polymerization initiator that are added if needed, An alcohol system, an ester system, an ether alcohol

system, a ketone system, a hydrocarbon system, Although high polar solvents, such as an aromatic solvent and dimethylformamide (DMF), the solvent in particular that contains a small amount of water in them depending on the case, etc. are not limited, it distributes or dissolves in the solvent of independent or mixed stock chosen from a viewpoint of solubility or uniform coating nature uniformly, and becomes a paint.

[0059]For the homogeneity of coating, and the improvement in adhesion, a surface-active agent, a leveling agent, a coupling agent, and polymer can also be added to the above-mentioned paint.

[0060]As for the paint prepared as mentioned above, a spin coat method, a dip method, the die coat method, the bar coat method, a spray method, the roll coat method, the meniscus coating-machine method, flexo print processes, screen printing, the bead coating-machine method, etc. are raised. As a substrate which forms the thin film or antireflection film of this invention, Polymethylmethacrylate (PMMA), polycarbonate (PC), Polyethylene terephthalate (PET), diethylene-glycol bisallyl carbonate, Polyether sulphone (PES), styrene/maleic acid resin, styrene/acrylonitrile copolymer, Polychlorostyrene, polyacid-ized vinylidene, polyarylate, vinyl chloride resin, Transparent resin, such as polystyrene resin, polyethylene terephthalate (PET), Triacetyl cellulose (TAC), diacetyl cellulose, polyethylene, Diacetyl cellulose, acetate-butylate cellulose, polyether sulphone, A poly acrylic resin film, a polyurethane system resin film, a polycarbonate film, Although films, such as a polysulfone film, a trimethyl pentene film, a polyether ketone film, an acrylonitrile (meta) film, polypropylene, and a VCM/PVC film, glass, etc. are raised, it is not limited in particular.

[0061]The thin film or acid-resisting article like especially recent years and this invention, It is used for manufacture of the pasting film for the transparent substrate, the polarizing plate, guard plate and light filter which are used for a liquid crystal display, or the use in many cases, and also in a film application with easy coating of a large area The sake, It is applied suitably for Tori or a diacetyl cellulose film, a saponification processing triacetyl cellulose film, or a polyethylene terephthalate film.

[0062]Although the thin film of the invention in this application is suitably used as an optical thin film, the optical thin film refers to the thin film which a beam of light crosses on the boundary where refractive indicees differ, and causes interference here, when a beam of light enters into the substrate with which the thin film exists in the upper part. In an optical thin film, catoptric light appears as an interference light of incident light. For example, a part of incidence catoptric light reflects a transparent optical thin film on a transparent substrate on the boundary of air and a thin film at the time of 1 formation beam, a part is reflected by the thin film and a substrate interface, and catoptric light turns into those interference lights as a whole. An interference light makes the reflectance of a substrate reduce or increase as a result. An optical thin film is thin to such an extent that light causes interferential action, and it depends

for the reflectance of a substrate on the refractive index and thickness of an optical thin film. [0063]Although the invention in this application is not limited in use, it is one of the purposes to provide the optical thin film of a low refractive index mainly for the purpose of reduction of reflectance, and the thickness of a low refractive index layer, When the refractive index of lambda and this layer is set to n for the wavelength of the light which wants to reduce reflectance, it is preferred that it is an integral multiple ($\lambda/4n$). Usually, since it is preferred to set lambda as 500-550 nm since it is aimed at a light region, 80-130-nm 85-115 nm of thickness 70-200-nm is still more preferably good more preferably. Since it may become insufficient decreasing of the reflectance by the light interference in a light region and it remains only in reduction of the reflectance by the refractive index of a base material surface being low when thickness is less than 70 nm, or when exceeding 200 nm, compared with the case where an optical thin film is provided, reflectance becomes high, and the acid-resisting effect is inferior. However, in particular when using, for example as a low dielectric, it may not be limited to such thickness, but it may be about 10 nm in thickness.

[0064]It is known that performance will be improved when the acid-resisting operation by a low refractive index film laminates the multilayer film from which a refractive index differs by optical film thickness. When using as a composition film of a multilayer cascade screen, the layer of a high refractive index can be provided rather than this low refractive index film as a lower layer of this low refractive index film. Also in this invention, if a high refractive index layer higher than the refractive index of a transparent substrate or a hard court layer is provided in the middle of a transparent substrate or a hard court layer, and this low refractive index film, it is possible to improve the performance of an acid resistibility article more. In this case, it is called for 1.56 or more with the value which the refractive index of the high refractive index layer measured by the D line in 20 ** that it is 1.6 or more preferably.

[0065]. [whether a high refractive index layer forms conductive compounds, such as titanium oxide and tin dope indium oxide (ITO), in a film by the vacuum deposition method or a sputtering technique, and] To organicity, an inorganic binder, or both mixed stock binder, antimony oxide, It obtains by forming the thin film which distributed the metallic-compounds ultrafine particle with high refractive indicees, such as a selenium dioxide, titanium oxide, the tin oxide, antimony dope tin oxide, phosphorus dope tin oxide, a zinc oxide, zinc antimonate, and tin dope indium oxide. Although this invention is not limited, as an organic binder, an epoxy resin hardened material, the resin which carried out radical crosslinking polymerization, etc. are used, and the hydrolysis hardened material of the Silang system compound, etc. are used as an inorganic system binder.

[0066]As for the thickness of a high refractive index layer, when the refractive index of lambda and this layer is set to n for the wavelength of the light which wants to reduce reflectance, it is preferred that it is an integral multiple ($\lambda/4n$). Although based also on a membranous

refractive index, specifically, 90-400 nm is the range of 110-180 nm more preferably.

[0067]The ultrafine particle used for a high refractive index layer The tin oxide, the antimony dope tin oxide, When it has conductivity like the phosphorus dope tin oxide, zinc antimonate, and tin dope indium oxide and the high refractive index layer itself has conductivity of 10^{10} - 10ohms / ** grade, an antistatic function and since an electromagnetic wave shielding function can be given further, it is desirable on acid resistibility articles. Here, conductivity refers to the sheet resistance measured according to JIS K6911.

[0068]Abrasion-proof nature may be required by the substrate depending on a use. Although aimed at a resin base material in many cases, a hard court layer is provided between a substrate and a low refractive index film by the wet coat method as a means which improves the abrasion-proof nature of a substrate. Usually, in a hard court layer to organicity, an inorganic system binder, or both mixed stock binder. The particles of metallic compounds, such as oxidized silicon, antimony oxide, a selenium dioxide, and titanium oxide, i.e., ***** which generally added the particles of particle diameter smaller than the wavelength of visible light, are used as occasion demands. Although the hydrolysis hardened material of the Silang system compound, etc. have an epoxy resin hardened material which was described previously, the resin which carried out radical crosslinking polymerization, etc. as an inorganic system binder as an organic binder, there is no restriction in particular.

[0069]A hard court layer is formed in about 0.5-10-micrometer thickness, and can usually aim at the balance of an abrasion-proof function and other performances (for example, prevention from a crack generation).

[0070]In order to give the performance of the difficulty of becoming dirty, such as fingerprint dirt at the time of use, and the ease of wiping off, stain-proofing barriers, such as a fluorine system and a silicone series, may be provided in a low refractive index film.

[0071]

[Example]Although an example is furthermore given and this invention is explained concretely, it is not limited to this. The evaluation methods and the measuring means which were used in the following examples and reference examples are as follows.

[0072]a. refractive-index and thickness: -- measured value b. one side reflectance: by an ellipsometer -- the reflectance measured value at 540 nm by a spectrophotometer -- the conductive hard court film was prepared according to the following reference examples 1-4.

[0073](Reference example 1) Gravure coating of solids concentration 20wt% of the following presentation paint was carried out to one side of the 80-micrometer-thick triacetyl cellulose film (made by Fuji Photo Film "FUJITAKKU"), after deliquoring, the 1000mJ exposure of the UV was carried out under the nitrogen purge, and the conductive hard court film was obtained.

[0074]

Cell NAKKUSU CXZ-300M1F (the Nissan chemicals company make and 230 weight-section

zinc antimonate 30wt% included methanol sol)

pentaerythritol -- doria -- KURIKRETO 30 weight sections the thickness of the amount part profit
**** hard court film of CG-907 (made by Ciba-Geigy) duplexs -- about 3 micrometers and

conductivity -- about -- 6×10^8 omega/**, and a refractive index were 1.66.

[0075](Reference example 2) Gravure coating of solids concentration 20wt% of the following presentation paint was carried out to one side of the 75-micrometer-thick polyethylene terephthalate film (made by Toray Industries, Inc. "lumiler"), after deliquoring, the 1000mJ exposure of the UV was carried out under the nitrogen purge, and the conductive hard court film was obtained.

[0076]

ELECOM W-32 (catalyst transformation shrine make and phosphorus dope oxidation 230 weight-section tin 30wt% included benzyl alcohol sol)

pentaerythritol -- doria -- KURIKRETO 35 weight sections the thickness of the amount part profit
**** hard court film of CG-907 (made by Ciba-Geigy) duplexs -- about 3 micrometers and

conductivity -- about -- 3×10^8 omega/**, and a refractive index were 1.67.

[0077](Reference example 3) On one side of an 80-micrometer-thick triacetyl cellulose film (made by Fuji Photo Film "FUJITAKKU"). Gravure coating of solids concentration 18wt% of the following presentation paint was carried out, after deliquoring, in 130 ** hot air drying equipment, it was made to react in 110 ** hot air drying equipment continuously for 20 seconds for 2 hours, and the conductive hard court film was obtained.

[0078]

Cell NAKKUSU CXZ-300M1F (the Nissan chemicals company make and 183 weight-section zinc antimonate 30wt% included methanol sol)

Epicoat 827 (oil recovery shell epoxy company make and 25 weight-section bisphenol A system epoxy resin)

Gamma-glycidoxypolytrimetoxysilane hydrolyzate Five weight sections Aluminium acetylacetonato As for the thickness of 5 weight-section profitable **** hard court film, 5×10^{10} omega/**, and the refractive index of about 3 micrometers and conductivity were 1.63 about.

[0079](Reference example 4) Gravure coating of solids concentration 20wt% of the following presentation paint was carried out to one side of the 75-micrometer-thick polyethylene terephthalate film (made by Toray Industries, Inc. "lumiler"), after deliquoring, in 160 ** hot air drying equipment, it was made to react and the conductive hard court film was obtained for 30 seconds.

[0080]

ELECOM W-32 (catalyst transformation shrine make and phosphorus dope oxidation 230 weight-section tin 30wt% included benzyl alcohol sol)

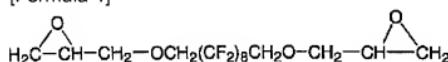
Trimethylopropane triglycidyl ether Five weight sections Gamma-glycidoxypolytrimetoxysilane hydrolyzate 25 weight sections Aluminium acetylacetonato The thickness of 5 weight-section profitable **** hard court film About 3 micrometers, About, conductivity was 2×10^8 omega/**, and the refractive index was 1.66.

[0081]Next, the low refractive index film was prepared according to the reference examples 5-11.

[0082](Example 1) Using the following presentation, solids concentration 1.5wt% of the paint was prepared with the organic solvent, gravure coating was carried out, after deliquoring, in 130 ** hot wind oven, it heat-hardened on condition of within a time [in which a substrate does not receive heat damage] (about 1 minute), and the low refractive index film was obtained.

[0083]

[Formula 1]



50 weight-section oxidized silicon particles (mean particle diameter of 10 nm) 50 weight sections Gamma-glycidoxypolytrimetoxysilane hydrolyzate 50 weight sections Aluminium acetylacetonato The thickness of 5 weight-section profitable **** low refractive index film was about 90 nm, and the refractive index was 1.35.

[0084](Example 2) Using the following presentation, solids concentration 1.5wt% of the paint was prepared with the organic solvent, gravure coating was carried out, after deliquoring, in 130 ** hot wind oven, it heat-hardened on condition of within a time [in which a substrate does not receive heat damage] (about 1 minute), and the low refractive index film was obtained.

[0085]

[Formula 2]

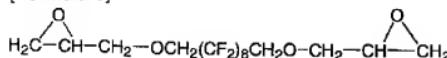


70 weight sections Magnesium fluoride (mean particle diameter of 15 nm) 50 weight sections Gamma-glycidoxypolytrimetoxysilane hydrolyzate 30 weight sections Aluminium acetylacetonato The thickness of 5 weight-section profitable **** low refractive index film was about 90 nm, and the refractive index was 1.32.

[0086](Example 3) Using the following presentation, solids concentration 1.5wt% of the paint was prepared with the organic solvent, gravure coating was carried out, after deliquoring, in 130 ** hot wind oven, it heat-hardened on condition of within a time [in which a substrate does not receive heat damage] (about 1 minute), and the low refractive index film was obtained.

[0087]

[Formula 3]

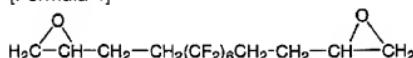


50 weight sections Oxidized silicon particles (mean particle diameter of 20 nm) 25 weight sections Gamma-glycidoxypropyltrimetoxysilane hydrolyzate 50 weight sections Aluminium acetylacetonato The thickness of 5 weight-section profitable **** low refractive index film was about 90 nm, and the refractive index was 1.33.

[0088](Example 4) Using the following presentation, solids concentration 1.5wt% of the paint was prepared with the organic solvent, gravure coating was carried out, after deliquoring, in 130 ** hot wind oven, it heat-hardened on condition of within a time [in which a substrate does not receive heat damage] (about 1 minute), and the low refractive index film was obtained.

[0089]

[Formula 4]



70 weight sections Oxidized silicon particles (mean particle diameter of 10 nm) 50 weight sections Gamma-glycidoxypropylmethyldietoxysilane hydrolyzate 30 weight sections Aluminium acetylacetonato The thickness of 5 weight-section profitable **** low refractive index film was about 90 nm, and the refractive index was 1.35.

[0090](Example 5) Using the following presentation, solids concentration 1.5wt% of the paint was prepared with the organic solvent, gravure coating was carried out, after deliquoring, in 130 ** hot wind oven, it heat-hardened on condition of within a time [in which a substrate does not receive heat damage] (about 1 minute), and the low refractive index film was obtained.

[0091]

[Formula 5]



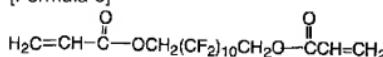
85 weight sections Oxidized silicon particles (mean particle diameter of 10 nm). 50 weight-section gamma-glycidoxypropyltrimetoxysilane hydrolyzate 15 weight sections Ethyl silicate hydrolyzate Five weight sections Aluminium acetylacetonato The thickness of 5 weight-section profitable **** low refractive index film was about 90 nm, and the refractive index was 1.37.

[0092](Example 6) Using the following presentation, solids concentration 1.5wt% of the paint was prepared with the organic solvent, gravure coating was carried out, after heating deliquoring, the 800mJ exposure of the UV was carried out under the nitrogen purge, and the

low-refractive-index hardening layer was obtained.

[0093]

[Formula 6]

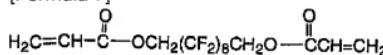


70 weight sections Oxidized silicon particles (mean particle diameter of 10 nm) 100 weight sections gamma-acryloyloxypropyl trimethoxysilane 30 weight sections CG907 The thickness of 4 weight-section profitable **** low refractive index film was about 90 nm, and the refractive index was 1.32.

[0094](Example 7) Using the following presentation, solids concentration 1.5wt% of the paint was prepared with the organic solvent, gravure coating was carried out, after heating deliquoring, the 800mJ exposure of the UV was carried out under the nitrogen purge, and the low-refractive-index hardening layer was obtained.

[0095]

[Formula 7]



40 weight sections Perfluoro octyl ethyl acrylate 20 weight sections Oxidized silicon particles (mean particle diameter of 10 nm) 100 weight sections gamma-acryloyloxypropyl trimethoxysilane 40 weight sections CG907 The thickness of 4 weight-section profitable **** low refractive index film is about 90 nm, The refractive index was 1.36.

[0096](Examples 8-35) The result of having applied the low refractive index film shown in Examples 1-7 to the substrate with a conductive hard court film obtained by the reference examples 1-4 is shown in a table.

[0097]

[Table 1]

実施例	参考例	基準性ハーフコードト板	低屈折率膜		片面反射率(%)
			屈折率	反射率	
8	1	1.66	1	1.35	0.7
9			2	1.28	0.3
10			3	1.33	0.6
11			4	1.35	0.7
12			5	1.37	0.9
13			6	1.32	0.5
14			7	1.36	0.8
15	2	1.67	1	1.35	0.5
16			2	1.28	0.2
17			3	1.33	0.4
18			4	1.35	0.5
19			5	1.37	0.7
20			6	1.32	0.3
21			7	1.36	0.6
22	3	1.53	1	1.35	1.0
23			2	1.28	0.5
24			3	1.33	0.9
25			4	1.35	1.0
26			5	1.37	1.2
27			6	1.32	0.7
28			7	1.36	1.0
29	4	1.66	1	1.35	0.7
30			2	1.28	0.3
31			3	1.33	0.6
32			4	1.35	0.7
33			5	1.37	0.9
34			6	1.32	0.5
35			7	1.36	0.8

With the one side reflectance said here, in order to lose reflection of a rear face, the surface reflectance of the test piece which painted the rear face black is measured with a spectrophotometer, and the average value of 500-600 nm is taken.

[0098]

[Effect of the Invention]By this invention, the thin film which was easily excellent in the acid resistibility which can be manufactured and the antireflection film using it, and an acid resistibility article can be provided.

[Translation done.]